CATION EXCHANGER MIXED MATRIX MEMBRANE (MMM) FOR LEAD (II) REMOVAL FROM WASTEWATER

NURUL FARHANA BINTI MOHAMED BASRI

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering

Signature	
Name of Supervisor	Dr Syed Mohd Saufi Bin Tuan Chik
Position	Senior Lecturer
Date	30 March 2012

ABSTRACT

Many toxic heavy metals have been discharged into the environment as industrial wastes everyday. In all over the world, industry is forced by the regulation body to diminish down the heavy metal content to the acceptable level in their wastewaters effluents. In the current research, cation exchanger mixed matrix membrane (MMM) was developed for the lead (Pb) removal from wastewater. A list of commercial cation resin was screened for highest Pb removal. These resins include Dowex M-31, Dowex MAC-3, Amberlite IR-120, Lewatit SP 112, Amberlite IRC-86, Lewatit TP-214, Amberlite IRN-150 and Dowex Marathon MSC. Dowex M-31 cation resin was incorporated into ethylene vinyl alcohol based polymer at different resin loading range from 10 – 30 weight % to prepare cation MMM. In a batch experiment, several parameters were optimized including Pb (II) concentration between 100 to 2000 mg/L, pH between 1 to 8, contact time between 3 to 12 hours and the amount of absorbent from 0.1 to 1 g. Adsorption isotherm for the cation MMM and ground resin were follow to Langmuir isotherm. The increase in resin loading will increase the binding capacity of cation MMM up to a limitation of 50 wt% resin loading. The concept of MMM was successfully expanded to the application of heavy metal removal.

ABSTRAK

Setiap hari banyak toksik logam berat telah dilepaskan ke alam sekitar sebagai bahan buangan industri. Di seluruh dunia, badan pengawal seliaan menghadkan pengeluaran kandungan logam berat ke tahap yang diterima dalam sisa buangan mereka. Di dalam penyelidikan ini, *mixed matrix membrane* (MMM) penukar cas positif telah di bangunkan untuk menyingkirkan plumbum (Pb) dari sisa air kumbahan. Beberapa jenis resin penukar cas positif komersial telah di uji untuk penyingkiran plumbum tertinggi seperti Dowex M-31, Dowex MAC-3, Amberlite IR-120, Lewatit SP 112, Amberlite IRC-86, Lewatit TP-214, Amberlite IRN-150 dan Dowex Marathon MSC. Dowex M-31 telah dicampurkan ke dalam polimer etilena vinilalkohol (EVAL) berdasarkan muatan resin yang berbeza-beza dari peratusan 10-30% berat cecair polimer untuk menyediakan MMM) penukar cas positif. Beberapa parameter telah dilakukan ujikaji seperti kepekatan Pb (II) antara 100 hingga 2000 ppm, masa penjerapan di antara 3-12 jam dan jumlah bahan penjerap antara 0.1-1 g. Ukuran penyerapan MMM penukar cas positif dan resin mengikut hubungan Langmuir. Peningkatan jumlah resin di dalam membran meningkatkan keupayaan muatan resin untuk penyikiran sehingga muatan maksimum 50% resin. Konsep MMM telah berjaya di luaskan dalam aplikasi penyingkiran logam berat.

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LIST OF ABBREVIATIONS

AAS	-	Atomic Absorption Spectroscopy
DMSO	-	Dimethyl sulfoxide
EVAL	-	Ethylene vinyl alcohol
MMM	-	Mixed Matrix Membrane

CHAPTER 1

INTRODUCTION

1.1 Background

Heavy metals are ordinary in industrial applications such as in the manufacture of pesticides, battery, alloys, electroplated metal parts, textiles dyes, and steel (Abo Farha et al., 2008). Many toxic heavy metals have been discharge into the environment as industrial wastes. Industry has been forced by the regulation authority to reduce the contents of heavy metal in their industrial wastewaters to the acceptance level. Excessive content of heavy metal in water or wastewater might give an adverse effect to the environment as well as human life such as kidney failure, nervous system damage and bone damage, and other serious illness (Sgarlata et al., 2008). Heavy metal toxicity can also result in break or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver and other vital organs. However, in small quantities, certain heavy metals are nutritionally important for a healthy life. These metals are commonly found naturally in foodstuffs.

Several methods has been developed for removal heavy metals from wastewaters such as precipitation, coagulation, complexing, solvent extraction, ion-exchange, electrochemical reduction and membrane processes such as reverse osmosis, nanofiltration and electrodialysis (Smara et al., 2005). Most of these processes however required continuous input of chemicals, high cost and even incomplete metal removal (Ismael et al., 2011).

Adsorption is a very efficient process for a variety of applications, and now it is considered an economical and effective method for metal ions removal from

wastewaters. In general, adsorption is the process of collecting soluble substances that are in a solution, on a suitable interface. The interface can be betweeen the liquid and a gas, a solid, or another liquid. Studies on the treatment of effluent bearing heavy metal have revealed adsorption to be a highly effective technique for the removal of heavy metal from waste stream and activated carbon has been widely used as an adsorbent. Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon.

The potential absorption method by using of mixed matrix membrane is affordable and economical for effluents containing metal ions. Mixed matrix membrane requires absorption agents to enhance its performance, thus increasing treatment cost. Therefore, the need of alternative low-cost adsorbents has prompted the search for new and cheap sorption processes for wastewater treatment, as these materials could reduce significantly the wastewater-treatment cost.

Cation exchange resin is gained a significant interest among scientist mainly due to their unique properties on ion exchange capability. Large deposits of cation exchange resin in many countries provide local industries some promising benefits, such as cost efficiency, since they are able to treat wastewater contaminated with heavy metal at low cost. This cation exchange can be an absorbent for mixed matrix membrane performance to remove heavy metal and also for repeated used by regenerate the cation exchange resin.

1.2 Problem Statement

Even though their large static adsorption capacity, conventional method involved in heavy metal chromatographic separations are generally not able to operate at high linear velocities of the mobile phase. The pressure drop over the column is high even for low flow rates, and increases during the process time due to bed consolidation and plugging. The pressure drop in conventional chromatographic columns with particles diameter of 2 µm is usually high, up to 25MPa (Borneman et al., 2006).

In the recent years, membrane chromatography has gained considerable interest in adsorption-based process. In membrane chromatography, a short and wide chromatographic column is used in which the adsorptive membrane is stacked or packed in the module. In separation, the diffusion of the molecule into the adsorbent determines the adsorption limits of macromolecules from a liquid phase by adsorption into the porous media. Unlikely to packed bed chromatography that depend on diffusional transport of solute molecule, membranes chromatography strongly controlled by convective transport of solute molecules. This results a shorter process times and could minimizes the denaturation of the products. An ideal membrane support for application in chromatographic separation processes should be microporous to provide free interactions of molecules with the support. The membrane should be chemically and physically stable to resist to the conditions of adsorption, regeneration and should posses functional groups which provide interactions like ion exchange and affinity between the support and the solute molecules.

1.3 Objective

The main objective for this research is to produce cation exchanger mixed matrix membranes that are capable for lead removal from wastewater.

1.4 Scope of Study

The main scopes of this research are:

(i) To screen the potential cation resin that can give high binding capacity to lead (II) removal from eight commercial cation resins.

(ii) To produce an ethylene vinyl alcohol (EVAL) based MMM with different cation resin loading range from 10% - 30%.

(iii) To determine adsorption isotherm for various type of absorbent including ground resin and MMM.

(iv) To study different type of regeneration solution such as HCl, H_2SO_4, NaCl for the regeneration of MMM after the binding process.

CHAPTER 2

LITERATURE REVIEW

2.1 Ion Exchanger

Ion exchange is a reversible chemical reaction where an ions, atom or molecule that has lost or gained an electron and thus attained an electrical charge from solution is exchanged for a similarly charged ion attached to a stationary solid particle. This attraction may take place by direct contact with free metal anions, but that mechanism may be also absorbed in the sorption of metal, as a result of the interaction of metal cations with ligands in the solution. Actually, the formation of complexes, with ligands and/or OH^- influences the speciation of metals ions and thus the sorption efficiency and taking mechanism (Eric Guibal, 2004). These solid ion exchange particles are either naturally happen inorganic zeolites or synthetically generates organic resins. The synthetic organic resins are the major types used today because their characteristics can be fitted to specific applications.

Based on all the chromatographic methods, the most common used techniques in downstream processing are ion exchange. It is occupied for recovery and purification of proteins, polypeptides, nucleic acids, polynucleotides and other biomolecules. Ion exchange is advantageous in terms of wide applicability, high declaration and large adsorption capacity in large-scale protein purification processes. Another advantage of this technique is that the regeneration takes place under mild conditions (Saiful et.al., 2006).

2.2 Resin Types

There are variety of commercial ion exchange resins are available and have been applied in protein capturing, purifying and polishing steps (Saiful et al., 2006). Resins currently available exhibit a range of selectivity's and thus have wide application. Ion exchange resins are classified as cation exchanger, which has positively charged mobile ion available for exchange, and anions exchanger, whose exchangeable ion are negatively charged.

Resin can be classified as strong or weak acid cation exchanger or strong or weak base anion exchanger. Some example, cation exchange resin particles, Amberlite IR-12 styrene-divinyl benzene type of resin has an ion-exchange capacity of 4.4 meq/g dry resin (Kiyono etal., 2003). Mono-Plus SP112, a strong acidic, macroporous, cation-exchange resin with an average diameter of 10 micron. (Zhang et al., 2005). The chelating ion exchanger with iminodiacetate functional groups, Lewatit TP-207 is suggested by the Bayer company for selective removal of metal ions, mostly Pb (II) ions (Dabrowski et al., 2004). Selectivity is a guideline to the new types of ion exchangers with specific affinity to definite metal ions or groups of metals. Higher selectivity can gives a great exchangeability as well as reversibility of the sorption-elution process towards Pb (II). Frequently, cation-exchange is jointed with precipitation for Pb (II) removal from wastes (Lee and Hong, 1995). It should be emphasized that in most cases ion exchange enables replacing the undesirable ion by another one which is neutral within environment.

Table 2.1: Selectivity of Ion Exchange Resins

Strong acid cation exchanger	Strong base anion exchanger
Barium	Iodide
Lead	Nitrate
Calcium	Bisulfite
Nickel	Chloride
Cadmium	Cyanide
Copper	Bicarbonate
Zinc	Hydroxide
Magnesium	Fluoride
Potassium	Sulfate
Ammonia Sodium	
Hydrogen	

2.3 Comparison Technologies for Heavy Metal Removal

Many of studies have been made to avoid increases of heavy metal ions to human body and damages to environment. Several methods have been used to remove heavy metal ions, for examples, chemical precipitation, ion-exchange, adsorption, membrane filtration, and electro-chemical treatment technology. Adsorption using ion exchange is an effective and economic method for heavy metal removal from wastewater.

Activated carbon is the common used adsorbent although it is quite expensive. Many researchers have tried to find easily available adsorbents and low-cost in terms of economics to remove heavy metal ions, for examples, agricultural wastes, plant wastes, zeolites, and clays. Biosorption of heavy metals from aqueous solutions is a rather new process that has been established as a very talented process in the removal of heavy metal contaminants. The benefits of biosorption are its elevated efficient in reducing the heavy metal ions and the reasonably priced of biosorbents. Although biosorbents are characteristic in wide sources, the researchers are still in the theoretical and

experimental phase (Kyong-Soo Hong et al., 2010). Table 2.2 shown summarize of technologies to remove heavy metal from wastewater.

Table 2.2: Comparison of technologies to heavy metal removal from wastewater

Method	Advantages	Disadvantages
Chemical precipitation	• Simple • Inexpensive	• Large amount of sludge produced • Disposal problem
Chemical coagulant	• Sludge settling • Dewatering	• High cost • Large consumption of chemicals
Ion-exchange	• High regeneration of materials • Metal selective	• High cost • Less number of metal ions removed
Electrochemical methods	• Metal selective • No consumption of chemicals • Pure metals can be achieved	• High capital cost • High running cost • Initial solution pH and current density
Adsorption Using activated carbon	• Most of metals can be removed • High efficiency (99%)	• Cost of activated carbon • No regeneration • Performance depends upon absorbent • Low efficiency
Adsorption Using natural zeolite	• Most metals can be removed • Relatively less costly materials	• Low efficiency
Membrane process and ultrafilteration	• Less solid waste produced • Less chemical consumption • High efficiency (>95% for single metal)	• High initial and running cost • Low flow rates • Removal (%) decreases with the presence of other metals

Source: Farouq et al (2010)

Solvent extraction, or liquid ion exchange removes the metal by contacting the solution with an organic reagent that will react with the metal ion and result in its exchange to a dissolved form in the solvent. For optimum operation, this method needs high initial metal concentrations and the environmental standards for acceptable metal levels in discharged water cannot be met with this method alone. It is more to operate it

with other treatment systems such as membranes. Solvent extraction of metals is commonly working for selective recovery (Mack et al., 2004).

Conventional ion exchange resins have been used with solvent extraction in the recovery of metals. The simple phase separation and high concentration efficiency of ion exchange pretence the disadvantages of solvent extraction, mainly the difficulty in phase separation. However, these ion exchangers are insufficient selective to remove certain metals from large volumes of additional metals and thus metal-selective resins are being constructed. Disadvantages of these methods are relatively expensive, requiring complicated equipment with high operation costs, such as the regeneration and / or disposal of the regeneration liquid and the spent resin, and large energy requirements. Resin usage causes a large environmental burden in terms of disposal (Lee et al., 1998).

Chemical precipitation is still the simplest and cheapest means of removing metals from solution. The increase in pH caused by the precipitant results in the immobilization of the metal ions in insoluble forms, either as a metal hydroxide or a metal sulphide (Eccles, 1999). Sodium hydroxide introduces the least amount of inert material to the sludge, but this becomes expensive in the long-term, as large volumes of effluent and metal-laden sludge are produced and must be treated daily (Van Hille et al., 1999).

Membrane processes involving the removal of heavy metals from solution are mainly limited to those that require a membrane as a pretreatment filtration device linked to a second removal mechanism. An example of this is a combination of membrane technology and solvent extraction suggested by Kentish and Stevens (2001) in which metal is removed from industrial wastewater. In this example, the membrane is placed between the waste stream and the solvent stream and mass transfer of the selected chemical species occurs across the membrane into the solvent (Mack et al., 2004).

2.4 Membrane Process Use for Heavy Metal Removal

Membrane separation have been earlier used in order to retain metallic cations and the filtration was performed using chelating reagents as additives in the feed by increasing the size of the solute to be retained. In ultrafiltration, the more often used chelating polymer are poly-acrylic acid and polyethylenimine and their derivatives but natural chelating ligand as alginate and chitosan were also used. The filtration assisted by complex formation is extended to nanofiltration. In such type of filtration, the chelating ligand had to be regenerated in the final step of the process, before recycling, in order to minimise waste amounts. Consequently, to overcome this step, the recent studies involve membranes bearing the chelating groups (Anne Bougen et al., 2001).

Reverse osmosis membranes used have an opaque barrier layer in the polymer matrix where most separation occurs. Mostly, the membrane is designed for water to pass through this dense layer while preventing the passage of solutes (such as salt ions). This process needs a high pressure to be applied on the high concentration side of the membrane (Bakalár et al., 2009).

CHAPTER 3

METHODOLOGY

3.1 Materials

EVAL (a random copolymer of ethylene and vinyl alcohol) with an average ethylene content of 44 mol% was purchased from Aldrich and was used as membrane material without further modification. Dimethylsulfoxide (DMSO, Merck) was employed as solvent and 1-octanol (Fluka) as non solvent additive in the casting solution. Water was used as non-solvent in the coagulation bath. Commercial cation resin which are Dowex M-31, Dowex Marathon MSC, Dowex Mac-3 (Sigma-Aldrich), Amberlite IR 120, Amberlite IRN 150, Amberlite IRC 86, Lewatit MonoPlus TP 214 and Lewatit MonoPlus SP 112 (Fluka) were used as a potential adsorbent particle in screening experiment. Resins were freeze-dried to remove moisture and then were grinded and fractionated down to a fraction with an average size of 45 µm. Hydrochloric acid (HCl), sulfuric acid (H_2SO_4) was purchased by Fisher Chemical and sodium chloride (NaCl, Merck) are used for the regeneration of MMM adsorbers. Lead (II) solution was prepared by dissolving lead (II) nitrate ($PbNO_3$) powder in water.

Buffer solutions were freshly prepared in ultra pure water. Ultra purewater was prepared using a Millipore purification unit Milli-Q plus. The buffers used for washing were phosphate buffer at pH 7.

3.2 Resin Screening

The list of resin used in screening experiment is showed in Table 3.1.The resin was freeze dried and then grinded using ultra centrifugal grinder to obtain a particle fraction small than 0.45µm.

Approximately 0.05g dried ground resin was used in the screening experiment with triplicate run. The resin was equilibrate with phosphate buffer solution (pH 7) for about 3 hours in centrifuge test tube. The buffer was removed by centrifugation at 12000 rpm about 20 minutes to settle down the resin. Lead (II) nitrate solution (1000 ppm) was added to the tube and bind on rotator for about 12 hours. The remaining lead concentration was checked by atomic absorption spectrometer (AAS). The binding capacity for each resin is expressed by the amount of lead bound per gran of resin used.

Table 3.1 List of Commercial resin

Commercial resin	Functional Group	Matrix
LewatitMonoPlus TP214	Thiourea	Styrene divinylbenzene, macroporous
LewatitMonoPlus SP112	Sulfonic acid	Crosslinked polystyrene
Amberlite IRN 150	Sulfonic acid	Styrene divinylbenzene copolymer
Amberlite IR 120	Sulfonic acid	Styrene divinylbenzene copolymer
Amberlite IRC 86	Carboxylic acid	Gel polyacrylic copolymer
Dowex Mac-3	Carboxylic acid	Polyacrylic, macroporous
Dowex M-31	Sulfonic acid	Styrene divinylbenzene, macroporous
Dowex Marathon MSC	Sulfonic acid	Styrene divinylbenzene, macroporous

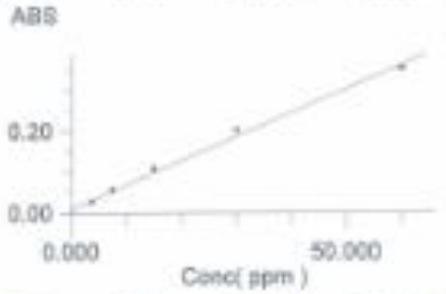
Table of Each Element 1/15/2012 10:48 AM

Analysis Mode : Flame/Manual
Analysis Name : Sample Analysis
Comment : MMM 20%

Meas. Date : 1/15/2012 10:48 AM
Element : Pb STD Unit : ppm UNK Unit : ppm

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
STD1		0.000	*****	0.0000	-0.0214
STD2		3.750	1.11	0.0270	-0.0471
STD3		7.500	0.72	0.0553	-0.0604
STD4		15.000	0.37	0.1083	-0.0665
STD5		30.000	0.54	0.2023	-0.0661
STD6		60.000	0.34	0.3537	-0.0557

Coefficient : K3=–
K2=–
K1=5.885297E-003
K0=1.040671E-002
Corr.Coef. : 0.9968



UNK-001	M 900 20%	156.73	0.03	0.9328	0.2780
UNK-002	M 800 20%	156.29	0.06	0.9302	0.2319
UNK-003	M 700 20%	146.17	0.81	0.8707	0.1118
UNK-004	M 600 20%	124.93	1.36	0.7457	0.0234
UNK-005	M 500 20%	112.30	1.01	0.6713	-0.0116
UNK-006	M 300 20%	61.876	10.81	0.3746	-0.0615
UNK-007	M 100 20%	27.412	20.42	0.1717	-0.1115

Figure A.17 : Resin Loading Analysis Part II